



Selective removal of the ammonium-nitrogen in ammonium acetate aqueous solutions by catalytic wet air oxidation over supported Pt catalysts

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ABSTRACT

The selective removal of ammonia from industrial waste streams and the conversion of the organic matter to biodegradable compounds, without excessive mineralization of the carbon has been investigated over powder and pelletized titania- and zirconia-supported Pt catalysts in the wet air oxidation (WAO) of aqueous solutions at 200 °C under 36 bar of air, in batch and trickle-bed reactors.

Ammonium acetate was chosen as a model compound (58 mmol L⁻¹, Total Organic Carbon, TOC = 1392 mg L⁻¹, Total Nitrogen, TN = 812 mg L⁻¹). In the absence of any catalyst, very little ammonium was removed. With addition of a Pt catalyst supported, NH₄⁺ was completely eliminated from the reaction mixture and converted to dinitrogen with a selectivity higher than 97.5%. The treated effluent contained very low concentration of nitrates as a by-product. Interestingly, the platinum catalysts were very little active in the mineralization of the organic carbon, so that the effluent could be post-treated in a conventional biological plant. The catalysts showed the same performances over recycling experiments in a batch reactor. Moreover, the pelletized catalysts were shown to be stable upon preliminary continuous experiments in a trickle-bed reactor over a period of 350 h. The 3%Pt/TiO₂ catalysts were significantly more active than the 3%Pt/ZrO₂ catalysts in batch and continuous experiments.

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1. Introduction

The increasing industrialization and the population growth have caused tremendous contamination of surface waters during the last decades. As a consequence, the regulations regarding the environmental protection are getting stricter and stricter throughout the world. In particular, the control of nitrogenous compounds in treated effluents is important, because of their undesirable effects on the environment. Indeed, the presence of excessive nutrients in the wastewaters in the form of ammonium-nitrogen contributes to eutrophication of surface waters and show acute toxicity to aquatic species.

The ammonium-nitrogen in the wastewaters from many industries has become a prevalent problem. Some of these effluents contain organic pollutants which are not easily biodegradable and high concentration of ammonia that both imply a special treatment. Effluents from sludge digesters, tanneries, food processing, fertiliser manufacturing, slaughter houses, landfill leachates, etc., are some examples of wastestreams with high nitrogen content and gram concentrations of ammonium [1].

Biological and physicochemical treatments are conventionally used for removing ammonium-nitrogen from wastewaters [2].

The standard biological process, consisting of a combination of aerobic nitrification and anaerobic denitrification using specific bacteria, is the most developed approach when the ammonium concentration is lower than 100 mg L⁻¹ [3]. Domestic wastewaters fall within this range. Such biological process is economical, but it is not often so effective when high concentrations of ammonium-nitrogen are present, due to the shortage of the carbon sources for the denitrification stage. Also, nitrification does not accommodate well to shock loads of ammonia. A novel biological wastewater treatment process, called "Anammox[®]", which proceeds via a partial nitrification of ammonia and conversion of ammonium and nitrite directly into dinitrogen, has been developed and can be used for effluents with relatively higher ammonium concentration (>100 mg L⁻¹). The cost reduction compared to the conventional nitrogen removal is considerable. This technique is still young but it has already been proven in several full-scale installations [4].

Physical technologies also exist to treat substantial concentrations of ammonia in water, such as air or steam stripping [5], ion exchange [6,7], and membrane separation. In the air stripping process, ammonia might be removed from the water and transferred into the air by forcing the air flow through the water. Since ammonia may exist in the solution either as the non-ionized form (NH₃)

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and/or as the ionized form (NH_4^+), an efficient stripping requires a pH adjustment above 10 to prevent the formation of ammonium ions that cannot be stripped. Then, the ammonia in the air can be treated by neutralization with sulphuric acid, catalytic oxidation, and adsorption over granular activated carbon filters or incineration. The ion-exchange method is a reversible chemical reaction where the ammonium ion from the wastewater is exchanged for a cation of a solid material. The process is simple and easy to implement. However, exchangers usually have low ammonium adsorption capacity.

Technical alternatives for the ammonium removal from highly concentrated wastewater are though still necessary. The catalytic wet air oxidation (CWAO) offers an alternative method in the removal of the ammonium ions. The wet air oxidation (WAO) technology was initially developed to oxidize the biologically refractory organic pollutants into products with lower molecular weights that might be easily treated in a conventional wastewater treatment plant. In general, this aqueous-phase reaction takes place at temperatures between 150 and 320 °C under pressures ranging from 5 to 200 bar [8–12]. However, in addition to the short-chain organic acids, CO_2 and water, ammonia is also usually produced and appears as a stable end-product which is difficult to oxidize further. On the other hand, catalytic wet oxidation is known to increase the feasibility of the WAO technology using dedicated catalysts. Various catalysts (oxides and supported metals) have shown potential for the ammonia oxidation in the liquid phase [13–26]. Imamura et al. [13] have found that an Mn/Ce composite was more active than a Co/Bi catalyst at temperatures higher than 260 °C under 40 bar. Noble metal supported catalysts, such as Pd, Ru and Pt, have been reported as efficient catalysts for the ammonia removal with good selectivity to N_2 [16,18,19].

In this study, the treatment consisted in removing the undesirable ammonium nitrogen content from the industrial effluents and transforming the non-biodegradable organics into biodegradable compounds (such as acetic acid). After successful ammonium removal, wastewater could then be recycled in a conventional biological wastewater treatment plant. High dinitrogen selectivity is also needed to avoid undesired products such as nitrites and nitrates. Among the different noble metal catalysts already investigated on different ammonium-containing substrates, the Pt catalysts appeared as the most selective compared to the Ru catalysts for instance [22,27]. Moreover, as the organic fraction is concerned, the platinum based catalysts were usually less active than the ruthenium catalysts, in particular for the mineralization of the acetate [28–30]. Consequently, this paper deals with the platinum catalysts. They were supported over TiO_2 or ZrO_2 , which are both chemically stable under the acidic or alkaline conditions upon CWAO [31].

2. Experimental

2.1. Preparation and characterization of the catalysts

The TiO_2 and ZrO_2 commercial supports were respectively supplied by Millenium (TiO_2 DT51, BET surface area 90 $\text{m}^2 \text{g}^{-1}$, anatase) and Melcat Chemicals (ZrO_2 XZO 632/18, BET surface area 90 $\text{m}^2 \text{g}^{-1}$, monoclinic) as powders. The pelletized supports were provided by Saint Gobain Norpro (TiO_2 ST31119, BET surface area 39 $\text{m}^2 \text{g}^{-1}$, anatase; ZrO_2 SZ31163, BET surface area 52 $\text{m}^2 \text{g}^{-1}$, monoclinic + cubic). Before use, the pellets were further crushed and sieved in the 0.8–1.2 mm range for the continuous experiments, to respect the criterion D/d_p larger than 20, with D is the internal diameter of the tubular reactor and d_p is the particle diameter [32].

Platinum was introduced by incipient-wetness impregnation using an aqueous solution of H_2PtCl_6 , which concentration

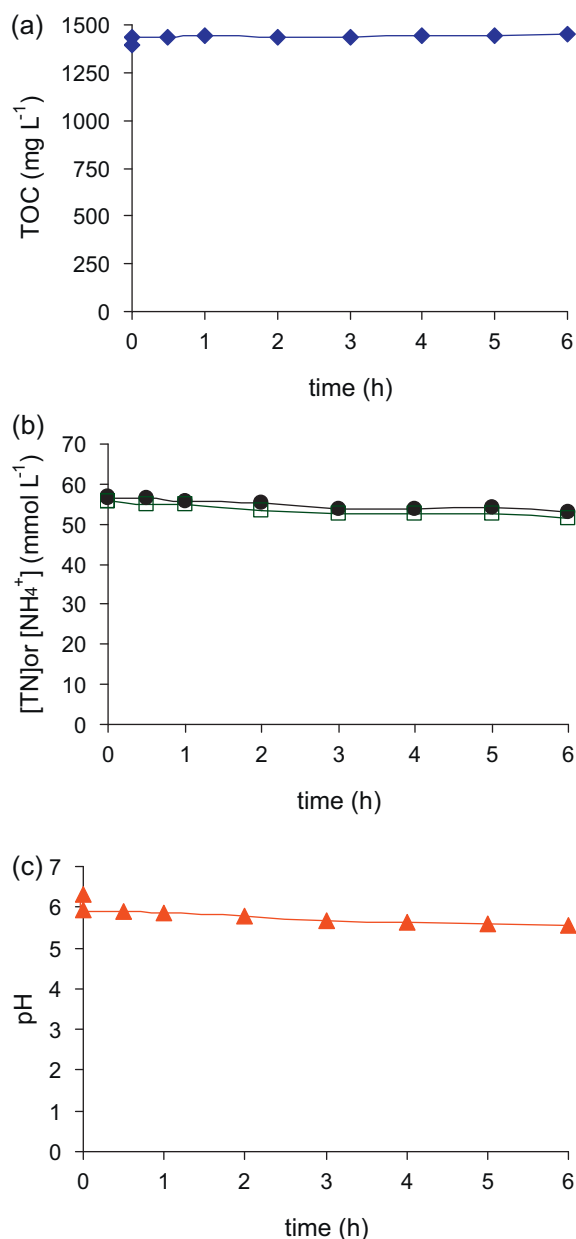


Fig. 1. Wet air oxidation of an ammonium acetate aqueous solution in the absence of any catalyst: evolution of the TOC (a), TN (●) and NH_4^+ (□) concentrations (b) and the pH (c) as a function of time. Reaction conditions: batch reactor, 150 mL ammonium acetate aqueous solution, 200 °C, 50 bar total pressure.

was accurately determined by ICP-OES (inductively coupled plasma-optical emission spectroscopy) before impregnation. The theoretical Pt weight loading was set at 3 wt%. The solids were then oven-dried at 120 °C overnight, and finally pre-reduced at 300 °C in flowing hydrogen (12 L h^{-1}) for 2 h in a tubular reactor. After cooling down to room temperature under H_2 , the cell was purged with argon and the catalyst was further passivated at room temperature under flowing 1% O_2/N_2 .

XRD characterizations were performed using a Siemens D5005 diffractometer with Cu K-radiation at 0.154184 nm. The samples were scanned in the 2θ range from 15° to 80°.

Transmission electron microscopy (TEM) direct observations were carried out on a JEOL 2010 microscope (200 kV, resolution 0.19 nm). The sample was prepared by suspending the powder in ethanol, deposition on a copper grid covered with a carbon film, and drying.

2.2. Catalytic oxidation reactions

Ammonium acetate solutions were prepared in deionized water and treated either in a batch autoclave or in a continuous tubular trickle-bed reactor.

Batch experiments were carried out in a 280 mL autoclave made of Hastelloy C22. In a typical run, the autoclave was loaded with 150 mL ammonium acetate aqueous solution (58 mmol L^{-1}) and 0.6 g catalyst. The reactor was flushed with argon in order to remove any trace of dissolved oxygen and the mixture was heated to the desired reaction temperature under gentle stirring. The reaction finally started by introducing the air pressure up to the predefined pressure and switching the stirrer on (1100 rpm). This point was taken as “zero time” for the reaction. Liquid samples were periodically withdrawn from the reactor (ca. 2 mL including purging), centrifuged to remove any catalyst particle in the liquid sample and further analysed after dilution.

The fixed bed reactor consisted of a 15 cm Hastelloy tube with an internal diameter of 1 cm, as described previously [33,34]. The ammonium acetate solution was injected down-flow using a HP pump. The air was also flowed downward together with the liquid feed. A back-pressure regulator was installed after the reactor.

The Total Organic Carbon (TOC) and Total Nitrogen (TN) contents in the liquid samples were also measured with a TOC-VCSH analyser coupled with a TN 171 unit (TNM-1) from Shimadzu. The inorganic carbon is converted into CO_2 by addition of HCl and purge with air. The non-purgeable TOC is then burnt in a catalytic oven at 680°C and the CO_2 which is produced is quantified using an IR detector. The TN was measured using a NO_2 -specific chemiluminescence detector. TN represents the total amount of nitrogen in the liquid phase, that is in our case only ammonium, nitrates and nitrites. The inorganic forms of nitrogen in the liquid phase (ammonium, nitrite and nitrate ions) were also analysed after dilution by a factor of 100 (ammonium ions) or 10 (nitrites and nitrates) using high performance ionic

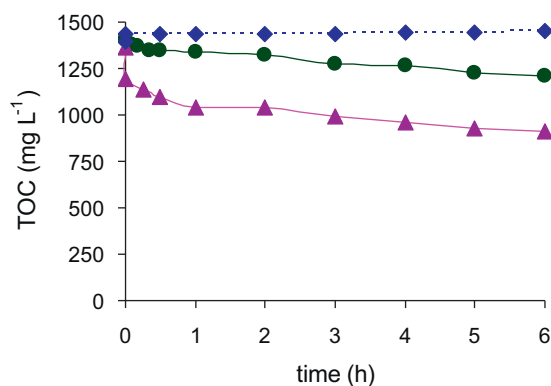


Fig. 2. TOC concentration as a function of time in the absence of any catalyst (♦) or in the presence of 3%Pt/TiO₂ (●) or 3%Pt/ZrO₂ (▲). Reaction conditions: batch reactor, 150 mL ammonium acetate aqueous solution, 200°C , 50 bar total pressure, 0.6 g catalyst.

chromatography (HPIC, Dionex) equipped with cationic (CS12A, $4 \text{ mm} \times 250 \text{ mm}$) and anionic (AS14A, $4 \text{ mm} \times 250 \text{ mm}$) columns. The eluents (1 mL min^{-1}) were H_2SO_4 22 mM for the cations and Na_2CO_3 8 mM/ NaHCO_3 1 mM for the anions analysis.

The pH values of the liquid samples were measured using a pH meter (Radiometer Analytical PHM240).

The metal leaching was measured via ICP-OES on the final reaction mixtures (Activa, Horiba JOBIN YVON).

3. Results and discussion

3.1. Blank experiments in the batch reactor

We first investigated the wet air oxidation of the ammonium acetate solution (58 mmol L^{-1}) without any catalyst. The oxidation was performed at 200°C under 50 bar total pressure (ca.

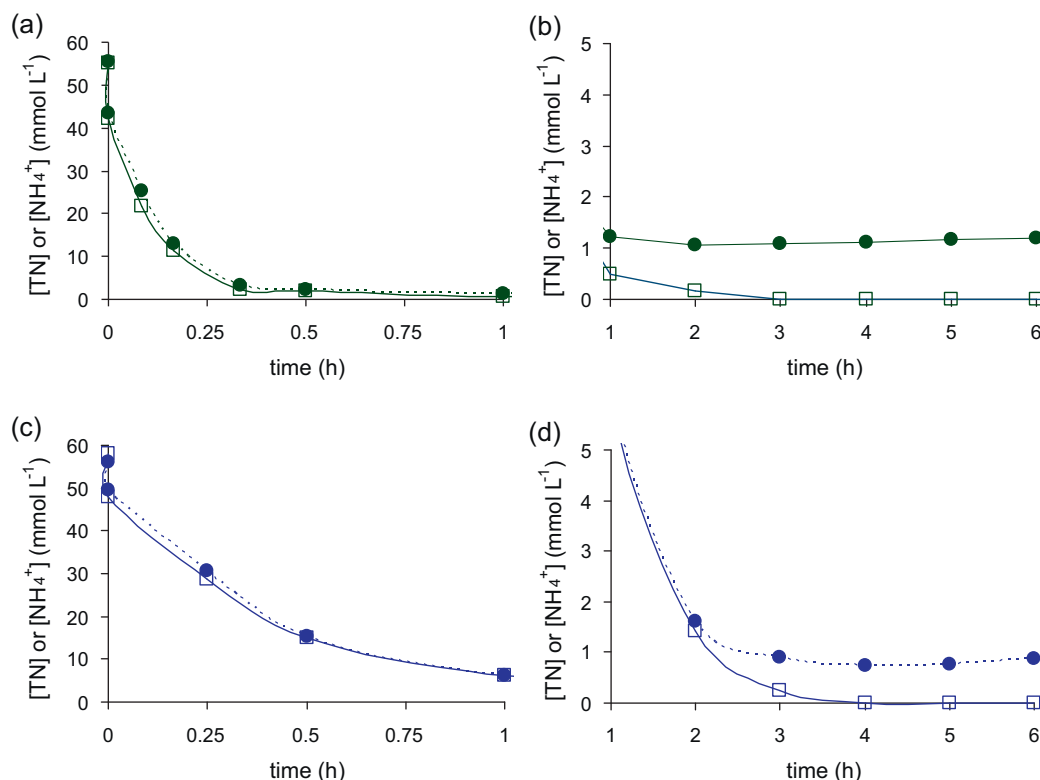


Fig. 3. Evolution of the TN (●) and NH_4^+ (□) concentrations in the presence of 3%Pt/TiO₂ (a, b) and 3%Pt/ZrO₂ (c, d). Reaction conditions: same as in Fig. 2.

7.2 bar oxygen partial pressure). This concentration of ammonium acetate corresponds to an initial TOC content of 1392 mg L^{-1} and $812 \text{ mg L}^{-1} \text{ NH}_4^+$. The evolution of the TOC, TN and ammonium concentrations and the pH during this 6 h experiment are shown in Fig. 1a–c.

When no catalyst was used, no change in the TOC value was observed (Fig. 1a). This observation is in agreement with the already reported data in the literature: acetic acid is often the main end-product formed upon the WAO of different pollutants. It is usually considered as refractory to further oxidation, even at temperatures as high as 200°C . The evolutions of TN and ammonium ions as a function of time are almost superimposed (Fig. 1b). Very little nitrogen was removed from the liquid phase in practice, even after 6 h reaction. The nitrogen content decreased by less than 5%. Accordingly, only traces of nitrite (maximum concentration $17 \mu\text{mol L}^{-1}$) and nitrate ions ($27 \mu\text{mol L}^{-1}$ after 6 h) were detected.

In the aqueous solution, ammonia may exist in either the non-ionized form (NH_3) and/or the ionized form (NH_4^+). The relative proportion of the two forms in aqueous solutions is mainly affected by pH and temperature, with a dissociation constant (pK_a) of $\text{NH}_4^+/\text{NH}_3$ equal to 9.25 at 25°C [35,36]. The pH of the freshly prepared ammonium acetate solution was 7. In the first sample withdrawn from the reactor when the temperature reached 200°C under argon, this value measured at room temperature under atmospheric pressure was ca. 6.3. After introduction of the air and upon oxidation the pH slightly decreased down to ca. 5.6. Since the reaction proceeded under acidic conditions, most of the ammonia occurs as the NH_4^+ ion, which cannot be stripped to the gas phase. It is then reasonable to speculate that the oxidation reaction essentially occurs in the liquid phase. This was further confirmed by the analysis of the reaction medium after cooling down the reactor. The final TN and NH_4^+ concentrations in the liquid phase were 54.8 and 53.6 mmol L^{-1} , respectively, and the pH was 5.8. These values are very close to the ones measured on the same samples withdrawn from the reactor at 200°C and under pressure (54.1 and 52.6 mmol L^{-1} , respectively for the TN and NH_4^+ concentrations, pH 5.6). Furthermore, after cooling of the reactor, the gas phase was scrubbed in a diluted sulphuric acid solution and was further analysed. No residual ammonium sulphate could be measured. We could conclude that stripping was negligible and that the ammonium concentration in the aqueous phase should represent all the unreacted ammonium.

Similarly, blank experiments were also performed in the presence of the bare TiO_2 or ZrO_2 supports. No significant conversion of the TOC, TN or NH_4^+ could be observed, showing that the supports did not exhibit any catalytic activity (not shown).

3.2. Catalytic performances in the batch reactor

The reaction was then performed in the presence of the $3\%\text{Pt}/\text{TiO}_2$ and $3\%\text{Pt}/\text{ZrO}_2$ catalysts. Fig. 2 shows the evolution of the TOC content as a function of time. The results for the ammonium and TN concentrations in the presence of $3\%\text{Pt}/\text{TiO}_2$ are shown in Fig. 3a during the first hour of the reaction; and in Fig. 3b during the next 5 h, with a different Y-axis. Likewise, Fig. 3c and d shows the results obtained in the presence of $3\%\text{Pt}/\text{ZrO}_2$.

A small decrease in the TOC concentration was observed at time zero in the presence of the Pt/ZrO_2 catalyst compared to the blank experiment, while the TOC content measured in the presence of Pt/TiO_2 at time zero corresponded to the initial concentration of the solution introduced in the reactor. This difference (14% of the initial TOC) may be due to some acetate adsorption on the ZrO_2 support. This adsorption was lower on the TiO_2 support, as already observed in the case of the phenolic pollutants such as p-coumaric acid [37], p-hydroxyphenylacetic acid or p-hydroxybenzoic acid [38], and 2-chlorophenol [39]. Under air pressure, the platinum catalysts were

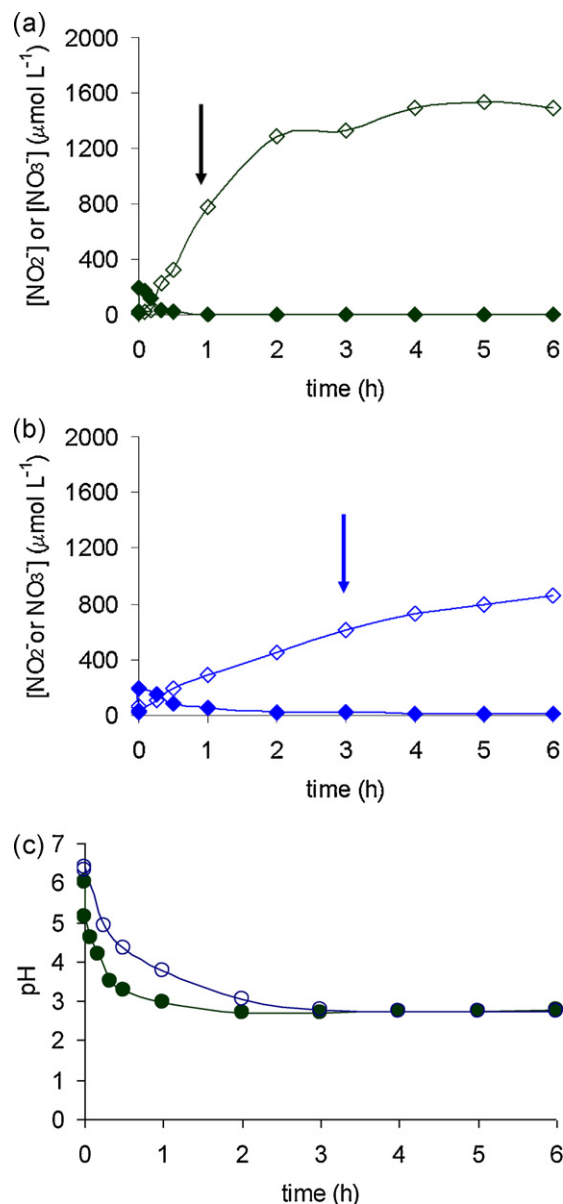


Fig. 4. Formation of nitrite (♦) and nitrate (◇) ions upon catalytic WAO of ammonium acetate in the presence of $3\%\text{Pt}/\text{TiO}_2$ (a) or $3\%\text{Pt}/\text{ZrO}_2$ (b) and evolution of the pH in the presence of $3\%\text{Pt}/\text{TiO}_2$ (●) or $3\%\text{Pt}/\text{ZrO}_2$ (○) (c). The arrows indicate 99% ammonium conversion. Reaction conditions: same as in Fig. 2.

poorly active in the mineralization of acetate, with a maximum TOC abatement of ca. 25% after 6 h of reaction, excluding the adsorption contribution to the overall abatement of the ammonium concentration. This result is consistent with earlier results reported in the literature [28–30].

On the other hand, the use of a platinum catalyst considerably promoted the conversion of ammonium which was rapidly converted to reach 99% conversion after approximately 1 h for the $3\%\text{Pt}/\text{TiO}_2$ catalyst and 2 h for the $3\%\text{Pt}/\text{ZrO}_2$ catalyst. The TN and NH_4^+ concentration profiles were very similar for both catalysts. This suggests that N_2 was by far the major end product, with an excellent selectivity. The gas phase was not directly analysed for N_2 , since it could be deduced from the TN balance, from the difference between the initial TN concentration introduced into the reactor and the TN concentration at a given reaction time. This assumption was consistent with the literature. It was earlier reported that in ammonia removal from aqueous solutions over different catalysts,

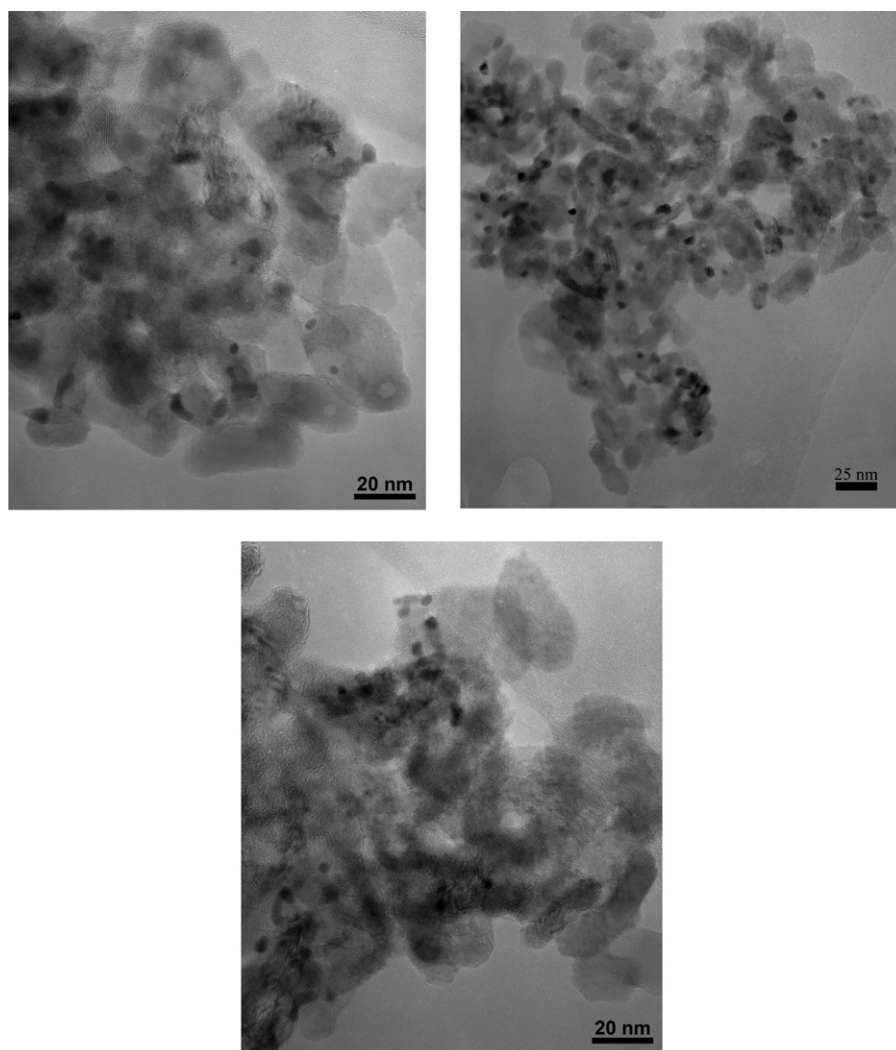


Fig. 5. TEM micrographs of the 3%Pt/TiO₂ catalyst.

the gas phase mainly contained dinitrogen with only trace amounts of NO_x [16,23].

The nitrogen atom balance between the NH₄⁺ and TN concentrations was examined in greater detail (Fig. 3b and c) after 1 h. One must note that they do not fit perfectly. While the ammonium has completely disappeared from the liquid phase, some TN was still measurable. Nitrogen is present in other forms, namely nitrite and nitrate ions. However, the amounts of TN and NH₄⁺ concentrations only differ by ca. 1–1.5 mmol L⁻¹.

To get more information about the reaction pathway, the formation of NO₂⁻ and NO₃⁻ was further analysed. The concentration profiles are shown in Fig. 4a and b.

Under the applied reaction conditions, only very small amounts of nitrites and nitrates were detected in the treated effluent. Nitrite ions were formed as an intermediate at the beginning of the reaction (maximum concentration 200 μmol L⁻¹), but rapidly got converted. The production of nitrate ions reached a constant concentration ca. 1.5 mmol L⁻¹ after 6 h in the presence of Pt/TiO₂, in line with the difference in the nitrogen balance previously observed in the liquid phase. Conclusively, the nitrogen balance is almost complete within ±3 at.%. The same observation holds for the Pt/ZrO₂ catalyst.

Additionally, the variation of nitrate concentration with the NH₄⁺ conversion provides some additional insight into the reaction mechanism. After the ammonium conversion reached 99%,

the nitrate concentration continued to increase slightly. Consequently, at high ammonium conversion, the remaining ammonium was quite significantly converted to nitrate. Another possibility is that the very low amount of NH₃, which might have been stripped to the gas phase, was solubilized back into the liquid phase and further selectively oxidized to nitrate. Nevertheless, this phenomenon only concerns less than 2% of the initial ammonium introduced in the reactor.

The results indicate that, compared with the Pt/TiO₂ catalyst, the Pt/ZrO₂ one exhibited a lower reaction rate. The reason for this difference is not yet understood. The texture of the two supports is very similar (*S*_{BET} ca. 90–92 m² g⁻¹, mean pore diameter 9 nm), the catalyst preparation method was the same, the XRD analysis suggested the presence of only small metal crystallites with XRD patterns identical to the ones of the bare supports. Additionally, the TEM observations did not reveal significant differences in the distribution and the dispersion of the metal particles (Fig. 5). Both catalysts showed average Pt particle sizes ca. 3–4 nm. A further investigation of the parameters to be controlled is certainly necessary, such as the acidity/basicity of the support. One may note that the point of zero charge (*pH*_{PZC}) is 6.1 for the ZrO₂ support, while it is 4.4 in the case of the TiO₂ support.

The pH variations were also monitored during the experiments (Fig. 4c). It was observed that the pH of the aqueous solution rapidly decreased at the beginning of the reaction, due to the ammonium

depletion and the formation of nitrites and nitrates. The pH values stabilized at a value of ca. 3. Such data confirm that, since the pH was acidic, most of the ammonia exists in the form of NH_4^+ , which is not stripped to the gas phase.

The present results showed that the NH_4^+ ions are very reactive under moderately acidic pH. This finding is in contradiction with some previous works which indicated that the waters need to be alkalized above pH 9 for an effective ammonia removal in the presence of different catalysts [13,16,17]. These authors noted that higher pH favoured the molecular form of ammonia in the aqueous phase and lead to higher reaction rates. For example, Imamura et al. [13] showed that the reaction did not proceed at all under acidic pH in the presence of the Co/Bi catalysts and only proceeded at pH over 9. In the work of Qin and Aika [16], in the presence of a $\text{RuO}_2/\text{Al}_2\text{O}_3$ catalyst at 230°C , the conversion of molecular ammonia was very high at alkaline pH, whereas under acidic conditions the NH_4^+ ions were only poorly reactive. Similarly, over a Cu/La/Ce composite oxide catalyst, higher pH yielded higher NH_3 removal [23]. Over a Ru/ TiO_2 catalyst, it was found that the ammonia solution needed to be alkalized above pH 12 to achieve high conversions [25]. In the treatment of a wastewater containing ammonia and phenol, the conversion of ammonia at 200°C was 52% and 88% for an initial pH of 5.6 and 12, respectively [40]. On the opposite, effective oxidation of aqueous ammonia at near neutral pH conditions at 160°C over a Pt/ TiO_2 catalyst was also reported, without prior alkanization of the water [41]. There is no consensus on that point.

3.3. Catalyst recycling

Recycling experiments were conducted with used catalyst samples in order to evaluate the re-usability of the platinum catalysts. After the first reaction run, the catalyst was recovered by filtration, washed with water, and dried overnight at 120°C . To compensate the loss of catalyst upon recovery, the first reaction run was repeated two times to recover sufficient catalyst to use the same amount of catalyst (600 mg) in the recycling experiments for a better direct comparison. The results are summarized in Fig. 7, for the titania supported Pt catalyst.

No recordable loss of activity was observed between the two consecutive runs. All the ammonium was still selectively transformed into molecular nitrogen. There was no increase in the amount of nitrates formed. The selectivity to N_2 was maintained at a level higher than 97.5%.

The same type of experiments performed on the zirconia supported catalyst is shown in Fig. 7. They also demonstrated that such catalysts might be reused without any degradation of the catalytic performances.

The metal leaching from the catalysts was examined by elementary analysis (ICP-OES) of the final solutions. The catalysts showed very good chemical stability with no detectable dissolution of Pt at the detection limit of the equipment ($<0.1 \text{ mg L}^{-1}$).

3.4. Impact of the platinum catalyst preparation method

The drying procedure during the preparation of the Pt catalysts was shown to affect the catalyst's performances. A series of catalysts was prepared using the same method as described above in Section 2, but, instead of drying the catalyst precursor in an oven before reduction under flowing hydrogen, the solid was dried in ambient air under the hood. The TOC abatement was very low over all catalysts. The comparison of the TN abatements depending on the drying procedure is shown in Fig. 8.

The ammonium conversion efficiency was higher than 98% within 1 h in the presence of the Pt/ TiO_2 catalyst dried at 120°C (Fig. 3), whereas it was only 28% within 1 h when the catalyst was dried in ambient air. Similarly, the TN abatements was 98% after

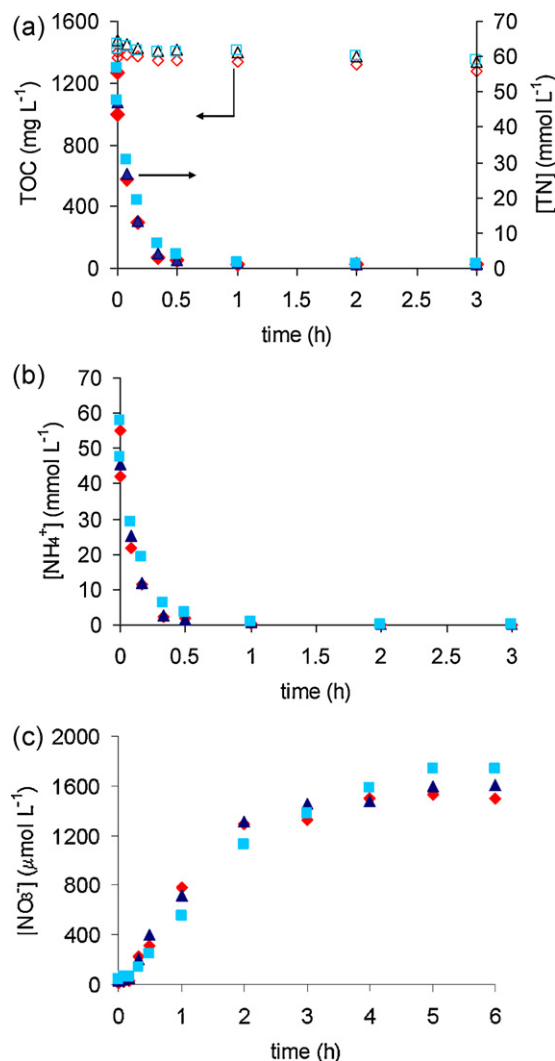


Fig. 6. Recycling experiments in a batch reactor in the presence of 3%Pt/ TiO_2 : TOC and TN concentrations (a), NH_4^+ concentration (b) and nitrate formation (c) as a function of time (1st run performed twice: \blacktriangle , \blacklozenge , \triangle , \diamond , recycling: \blacksquare , \square). Reaction conditions: same as in Fig. 2.

3 h over the Pt/ ZrO_2 catalyst dried at 120°C ; in contrast, it was only 28% after 6 h after drying in ambient air.

Fig. 9 presents the XRD patterns of the TiO_2 support and the two Pt/ TiO_2 catalysts dried at 120°C or in ambient air for comparison purposes.

The unlabeled peaks were assigned to the anatase phase of TiO_2 . It clearly appeared that drying at room temperature yielded much higher Pt crystallite sizes, which was detrimental to the activity. Indeed, as mentioned previously, in the oven-dried catalysts no discernable X-ray diffraction peak characteristic of platinum was detected (small particle size). In contrast, for the RT-dried catalyst, the intense Pt diffraction lines could be recorded. The same observations were made for the zirconia supported catalysts. The amounts of water remaining on the solids during the reduction step may be the reason for the different dispersions. Insufficient drying under ambient conditions may affect the reduction of the solids and may cause condensation of Pt precursors.

3.5. Stability of the catalyst upon continuous operation in a trickle-bed reactor

Finally, a series of tests was performed in a trickle-bed reactor to evaluate the stability of the catalysts. The experiments were

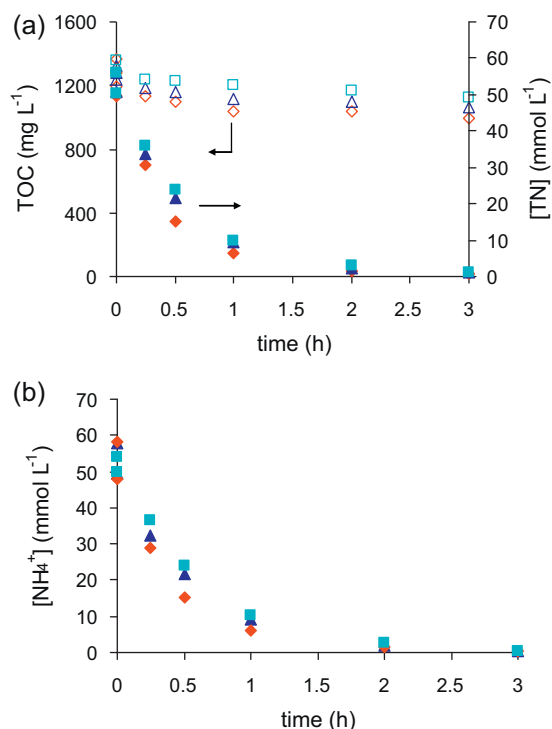


Fig. 7. Recycling experiments in the presence of 3%Pt/ZrO₂. See Fig. 6 caption.

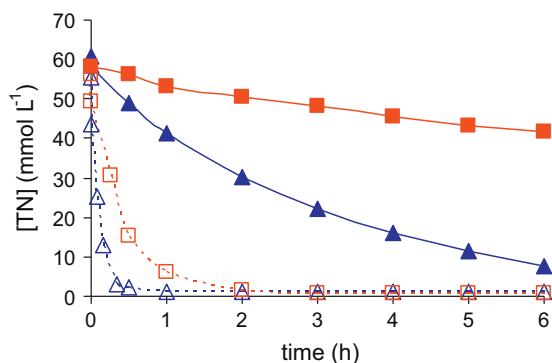


Fig. 8. Impact of the catalyst drying procedure on the catalytic performances. Pt/TiO₂ (△, ▲), Pt/ZrO₂ (□, ■), oven at 120 °C (△, □), ambient air (▲, ■).

performed at 200 °C under 50 bar total pressure with a fixed bed consisting of 1 g of catalyst diluted in glass beads. The ammonium concentration in the influent was kept constant at 58 mmol L⁻¹. The liquid flow rate was fixed at 30 mL h⁻¹ and the air flow rate was

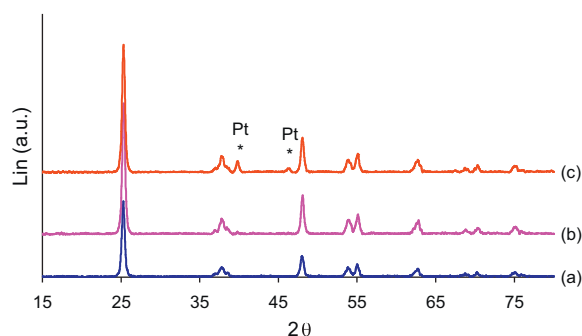


Fig. 9. X-ray diffraction patterns of the TiO₂ support (a), the 3%Pt/TiO₂ catalyst dried at 120 °C overnight (b) and the 3%Pt/TiO₂ catalyst dried in ambient air overnight (c).

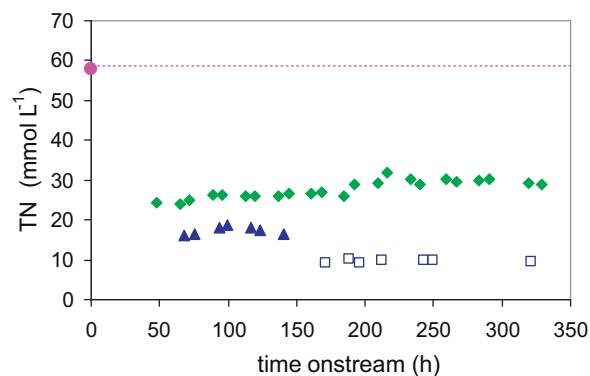


Fig. 10. Continuous catalytic wet air oxidation of an ammonium acetate effluent as a function of time on stream in a trickle-bed reactor. Initial TN concentration (●), TN concentration (◆) over 3%Pt/ZrO₂ (contact time = 1.055 h g_{Pt} g_N⁻¹), and 3%Pt/TiO₂ (▲, □) (contact time = 1.055 h g_{Pt} g_N⁻¹ and 2.11 h g_{Pt} g_N⁻¹, respectively).

kept constant at 5 L h⁻¹ STP. The effluent was periodically sampled and analysed in terms of residual TOC, TN and NH₄⁺ content. Fig. 10 presents the evolution of the TN concentration as a function of time on stream for a residence time of 1.055 h g_{Pt} g_N⁻¹.

After a few hours, the Pt/TiO₂ and Pt/ZrO₂ catalysts reached a stable TN conversion and no deactivation was observed during the tests. Again, the titania-supported catalyst showed higher ammonium conversion than the zirconia-supported catalyst. The results confirmed the very high selectivity of the platinum catalysts to dinitrogen (97.5%) all along the reaction. As the retention time of the influent stream was increased over Pt/ZrO₂ and set at 2.11 h g_{Pt} g_N⁻¹, an increase in the TN and ammonium removal was observed. The activity of the catalyst over time on stream was not affected.

In addition, the TOC removal was very low in line with expectations from experiments performed in batch mode (not shown). Further studies are still required to measure the ammonium removal efficiency and the selectivity as a function of residence time.

4. Conclusions

The objective of this work was to test different supported platinum catalysts in the CWAQ of industrial wastewaters, containing both organic matter and inorganic N-ammonium, to convert ammonium selectively to dinitrogen and minimize the organic carbon mineralization. This study demonstrated that the CWAQ of ammonium acetate in the presence of supported platinum catalysts is an interesting method for the treatment of wastewater containing high concentrations of ammonium. Very low formation of nitrite and nitrate ions was observed, since NH₄⁺ was very selectively converted into N₂ with selectivity higher than 97.5%. The organic carbon mineralization was minimized. The Pt/TiO₂ catalyst showed the best activity in batch and trickle-bed reactors at 200 °C under 50 bar total pressure. The catalysts could be recycled without modification of the activity and the selectivity. The continuous experiments confirmed the high stability of such catalysts under the chosen operating conditions. CWAQ can be considered as a potential pre-treatment before a biological stage in order to remove the residual amount of nitrates formed upon reaction.

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